

ELECTROPLATED QUATERNARY ALLOYS

FIELD OF THE INVENTION

The present invention generally relates to quaternary alloys containing at least nickel and cobalt that may be employed in place of chrome and chrome alloys and methods of making the quaternary alloys.

BACKGROUND OF THE INVENTION

Chromium is steel-gray, lustrous, hard, metallic, and takes a high polish. Chromium is a naturally occurring element present in the environment in several different forms. The most common forms are chromium (0), chromium (III), and chromium (VI). The metal chromium, which is the chromium (0) form, is used for making steel. Chromium (VI) and chromium (III) are often used for chrome plating. Chromium (VI) is used as an anti-corrosion treatment and as an electrical shielding material for certain sheet metals. There are many desirable characteristics associated with chromium plating.

However, the use of chromium (VI) and its compounds are restricted in certain applications in some areas, primarily in the European Union. Broad legislative restrictions such as the Restriction of Hazardous Substances in the United States are expected to eliminate the use of chromium (VI) compounds in electronic products by 2006. Substitutes for chromium, especially in the plating industry, are therefore desired.

SUMMARY OF THE INVENTION

The following presents a simplified summary of the invention in order to provide a basic understanding of some aspects of the invention. This summary is not an extensive overview of the invention. It is intended to neither identify key or critical elements of the invention nor delineate the scope of the invention. Rather, the sole purpose of this summary is to present some concepts of the

TASKP104US

invention in a simplified form as a prelude to the more detailed description that is presented hereinafter.

The present invention provides quaternary alloys containing at least nickel and cobalt that have a mirror bright deposit and a hardness on par with chrome.

5 At least two of many other alloy metals, such as iron and boron, are also contained in the quaternary alloys. In this context, the quaternary alloys contain at least four metal components. The desirable characteristics of the quaternary alloys made in accordance with the present invention are, at least in part, attributable to the use of certain brighteners in the electroplating bath. The
10 brighteners facilitate deposition of metal ions on the cathode in such a manner as to result in electroplated nickel cobalt quaternary alloys having numerous desirable properties. For example, the brighteners facilitate deposition of metal ions at relatively low current densities, thereby increasing the bright plating range. Consequently, the nickel cobalt quaternary alloys may take the place of
15 electroplated chrome and chromium alloys, thereby providing potential environmental benefits.

One aspect of the invention relates to methods of electroplating a quaternary alloy containing nickel cobalt involving providing an electroplating bath containing an anode, a cathode, water, ionic nickel, ionic cobalt, at least two
20 ionic alloy metals, and at least one brightener selected from the group consisting of sulfur containing brighteners and organic brighteners; and applying a current so that the quaternary alloy forms on/at the cathode.

To the accomplishment of the foregoing and related ends, the invention comprises the features hereinafter fully described and particularly pointed out in
25 the claims. The following description and the annexed drawings set forth in detail certain illustrative aspects and implementations of the invention. These are indicative, however, of but a few of the various ways in which the principles of the invention may be employed. Other objects, advantages and novel features of the invention will become apparent from the following detailed

description of the invention when considered in conjunction with the drawings.

BRIEF SUMMARY OF THE DRAWINGS

Figure 1 illustrates a schematic diagram of a nickel cobalt boron alloy electroplating system in accordance with one aspect of the present invention.

5 DETAILED DESCRIPTION OF THE INVENTION

The present invention provides quaternary alloys made by electroplating that exhibit two or more of high brightness, high luster, level/smoothness, uniform thickness, high hardness, high reflectivity, ductile, high density, resistant to corrosion, resistant to heat, and resistant to wear. Typically, the quaternary
10 alloys made in accordance with the present invention have a mirror bright deposit and a hardness on par with chrome. Electroplating involves metal in ionic form migrating in solution from a positive electrode (anode) to a negative electrode (cathode). The anode and cathode are connected to a power source and an electrical current is passed through the electroplating bath or solution
15 causing substrates at the cathode to be coated by the metal (nickel, cobalt, and at least two alloy metals) in solution. In most embodiments, the substrate to be plated is the cathode.

The cathodes are any electrically conductive material that can accommodate a nickel cobalt quaternary alloy plating while resisting degradation
20 by the acidic nature of the catholyte. The cathode substrates include metal structures and non-metal structures. Metal structures, or structures with a metal surface contain surfaces of one or more of aluminum, bismuth, cadmium, chromium, copper, brass, gallium, germanium, gold, indium, iridium, iron, lead, magnesium, nickel, palladium, platinum, silver, steel, stainless steel, tin, titanium,
25 tungsten, zinc, alloys thereof, and the like. Non-metal structures include plastics, circuit board prepregs (including materials such as glass, epoxy resins, polyimide resins, Kevlar®, Nylon®, Teflon®, etc.), ceramics, metal oxides, and the like.

TASKP104US

The electroplating bath is typically an aqueous solution. In addition to water, the electroplating bath (or the catholyte and anolyte if a separator is employed) may optionally contain one or more co-solvents. Such co-solvents include water-miscible solvents such as alcohols, glycols, alkoxy alkanols, ketones, and various other aprotic solvents. Specific examples of co-solvents include methanol, ethanol, propanol, ethylene glycol, 2-ethoxy ethanol, acetone, dimethyl formamide, dimethyl sulfoxide, acetonitrile, and the like.

Prior to placing the substrate/cathode in the electroplating bath, it may be optionally pretreated, washed and/or activated. Pretreatment may include cleaning with alcohol and/or with an anionic solution. Washing may include an anodically cleaning in an alkaline solution in the presence of a negative current, rinsing in hot or cold distilled or deionized water, and/or immersing in an acid bath. Activation includes one or both of anodically activating by passing a negative current through an acidic activator bath and cathodically activating by passing a positive current through an acidic activator bath. An advantage of the cleaning process is that the substrate is free of contaminant, such as oxides when placed in the plating bath eliminating the possible need for sequestering agents to prevent precipitation or the formation of sludge in the electroplating bath.

In the electroplating bath, platable nickel, cobalt, and at least two alloy metals are present in ionic form, and in embodiments where one of the two alloy metals is boron, platable boron is present in ionic form or in an ionic complex. Although platable boron may be present in ionic form or in an ionic complex, it is henceforth referred to as ionic boron for brevity. Sources of ionic nickel, cobalt, and alloy metals are typically the corresponding nickel, cobalt, and alloy metal salts and optionally an anode that contains one or more of nickel, cobalt, and/or one or more of the alloy metals.

Examples of nickel and cobalt salts include nickel acetate, nickel acetylacetonate, nickel ethylhexanoate, nickel carbonate, nickel formate, nickel

TASKP104US

nitrate, nickel oxalate, nickel sulfate, nickel sulfamate, nickel sulfide, nickel chloride, nickel fluoride, nickel iodide, nickel bromide, nickel oxide, nickel tetrafluoroborate, nickel phosphide, cobalt acetate, cobalt acetylacetonate, cobalt ethylhexanoate, cobalt carbonate, cobalt nitrate, cobalt oxalate, cobalt sulfate, cobalt chloride, cobalt fluoride, cobalt hydroxide, cobalt iodide, cobalt bromide, cobalt oxide, cobalt boride, cobalt tetrafluoroborate, and hydrates thereof.

The two or more alloy metals are any metals that can be electroplated in a compatible manner with nickel and cobalt generally include transition metals.

Examples of transition metals include aluminum, antimony, bismuth, boron, copper, gallium, germanium, gold, indium, iridium, iron, lead, manganese, molybdenum, niobium, osmium, rhodium, ruthenium, scandium, silver, palladium, platinum, tantalum, thallium, tin, titanium, tungsten, vanadium, yttrium, zirconium, zinc, and the like.

Examples of alloy metal salts include aluminum salts such as aluminum acetate, aluminum bromide, aluminum chloride, aluminum fluoride, aluminum iodide, aluminum nitrate, aluminum oxide, aluminum phosphate, and aluminum sulfate; antimony salts such as antimony acetate, antimony bromide, antimony chloride, antimony fluoride, antimony iodide, antimony oxide, and antimony sulfide; bismuth salts such as bismuth chloride, bismuth fluoride, bismuth nitrate, bismuth acetate, bismuth methanesulfonate, bismuth oxychloride, and bismuth citrate; copper salts such as copper sulfate, copper polyphosphate, copper sulfamate, copper chloride, copper formate, copper fluoride, copper nitrate, copper oxide, copper tetrafluoroborate, copper trifluoromethanesulfonate, and copper trifluoroacetate; gold salts such as gold bromide, gold chloride, gold iodide, gold oxide, and gold sulfide; indium salts such as indium acetate, indium sulfate, indium phosphide, indium chloride, indium fluoride, indium bromide, indium nitrate, indium oxide, indium methanesulfonate, and indium trifluoromethanesulfonate; iridium salts such as iridium bromide, iridium chloride,

TASKP104US

and iridium oxide; iron salts such as iron acetate, iron citrate, iron sulfate, iron chloride, iron fluoride, iron bromide, iron nitrate, iron oxide, iron tetrafluoroborate, iron phosphate, iron oxalate, and iron iodide; molybdenum salts such as molybdenum acetate, molybdenum bromide, molybdenum chloride, molybdenum fluoride, molybdenum oxide, and molybdenum sulfide; niobium salts such as niobium bromide, niobium chloride, niobium fluoride, niobium nitride, and niobium oxide; palladium salts such as palladium acetate, palladium bromide, palladium chloride, palladium iodide, palladium nitrate, palladium oxide, and palladium sulfate; platinum salts such as platinum bromide, platinum chloride, platinum iodide, platinum oxide, and platinum sulfide; silver salts such as tin salts such as silver acetate, silver carbonate, silver sulfate, silver phosphate, silver chloride, silver bromide, silver fluoride, silver citrate, silver nitrate, silver methanesulfonate, silver tetrafluoroborate, and silver trifluoroacetate; tantalum salts such as tantalum chloride, citrate, tantalum fluoride, tantalum nitride, and tantalum oxide; tin salts such as tin acetate, tin ethylhexanoate, tin sulfate, tin chloride, tin fluoride, tin iodide, tin bromide, tin methanesulfonate, tin oxide, tin tetrafluoroborate, tin trifluoromethanesulfonate, tin pyrophosphate, titanium salts such as titanium bromide, titanium chloride, titanium fluoride, titanium iodide, titanium nitride, titanium oxide, and titanium sulfide; tungsten salts such as tungsten bromide, tungsten chloride, tungsten fluoride, tungsten oxide, and tungsten sulfide; and tin sulfide; zinc salts such as zinc acetate, zinc citrate, zinc sulfate, zinc chloride, zinc fluoride, zinc bromide, zinc nitrate, zinc oxide, zinc tetrafluoroborate, zinc methanesulfonate, zinc trifluoromethanesulfonate, and zinc trifluoroacetate; and hydrates thereof.

Specific examples of boron salts and boron containing compounds include boron nitride, boron trichloride, boron trifluoride, boron triiodide, boron tribromide, boron oxide, boron phosphate, dimethylamine borane, morpholine borane, dimethylamino borane, dimethylsulfide borane, t-butylamine borane, ammonia borane, N,N-diethylaniline borane, diphenylphosphine borane,

TASKP104US

dimethylaminopyridine borane, ethylmorpholine borane, methylmorpholine borane, 2,6-lutidine borane, morpholine borane, oxathiane borane, phenylmorpholine borane, pyridine borane, tetrahydrofuran borane, tributylphosphine borane, triethylamin borane, trimethylamine borane, borax, and hydrates thereof. Boron may alternatively be introduced into the electroplating bath by a boron containing acid, an amino-borane compound, and/or an amine-borane compound (collectively referred to as boron containing compounds). The boron containing acid does not include boric acid, as boric acid improves conductivity and/or is used as a pH adjuster. It is noted that the boric acid does not provide a significant portion of platable boron, although in some instances it may provide minor amounts of platable boron.

The anodes are electrically conductive materials, and optionally contain materials that can deliver one or more of nickel, cobalt, and/or one or more of the alloy metal ions into the electroplating solution. Accordingly, in one embodiment, the anode contains at least one or more of nickel, cobalt, any of the alloy metals, and optionally other materials. In this embodiment, the anode is a working anode. There is an economic advantage associated with generation of the quaternary metal alloy ions from the working anodes. In particular, compared to providing metal ions from a liquid concentrate (such as a nickel salt), the cost of one or more of nickel, cobalt, and the alloy metals via an anode is a fraction of that from the liquid concentrate (such as about one-quarter of the cost or less including about one-eighth of the cost). Solid working anodes are also advantageous in that they are markedly easier to handle, store, and transport, compared with liquid concentrates of one or more of nickel, cobalt, and alloy metal salts. In another embodiment, the anode is an inert anode containing materials such as iridium oxide, platinum, titanium, platinum-titanium, graphite, carbon, and the like.

The electroplating bath contains an amount of ionic nickel, cobalt, and at least two alloy metals to facilitate electroplating the quaternary alloy, typically, on

TASKP104US

the cathode. In one embodiment, the electroplating bath contains about 10 g/l or more and about 150 g/l or less of ionic nickel, about 0.5 g/l or more and about 70 g/l or less of ionic cobalt, and about 0.01 g/l or more and about 20 g/l or less of each of at least two ionic alloy metals. In another embodiment, the electroplating bath contains about 40 g/l or more and about 100 g/l or less of ionic nickel, about 1 g/l or more and about 30 g/l or less of ionic cobalt, and about 0.05 g/l or more and about 10 g/l or less of each of at least two ionic alloy metals. In yet another embodiment, the electroplating bath contains about 50 g/l or more and about 70 g/l or less of ionic nickel, about 3 g/l or more and about 6 g/l or less of ionic cobalt, and about 0.1 g/l or more and about 6 g/l or less of each of at least two ionic alloy metals.

In some instances, the ratio of one of the alloy metals to cobalt and/or the ratio of cobalt to nickel in solution is set to facilitate an orderly and high quality deposition of the quaternary alloy on the substrate. For instance, in one embodiment, the ratio of one of the alloy metals to cobalt is from about 1:4 to about 3:1 while the ratio of cobalt to nickel is from about 1:20 to about 1:5. In another embodiment, the ratio of one of the alloy metals to cobalt is from about 1:3 to about 2:1 while the ratio of cobalt to nickel is from about 1:15 to about 1:10.

In order to obtain a nickel cobalt quaternary alloy with desirable properties, it is necessary to employ at least one brightener. Two or more brighteners can be used. Although not wishing to be bound by any theory, it is believed that the active deposition of nickel, cobalt, and alloy metal species simultaneously is complex, due to differences in characteristics between these metals, and that the presence of at least one brightener as described herein facilitates the orderly plating of the metals on a substrate such that beneficial properties are realized.

The brighteners that may be employed in the nickel cobalt quaternary alloy electroplating bath include sulfur containing brighteners and organic

TASKP104US

brighteners. In one embodiment, the electroplating baths contain from about 0.001% to about 5% by weight of at least one brightener. In another embodiment, the electroplating baths contain from about 0.005% to about 2.5% by weight of at least one brightener. In yet another embodiment, the
5 electroplating baths contain from about 0.01% to about 1% by weight of at least one brightener.

In one embodiment, the quaternary alloy electroplating baths contain an effective amount of at least one sulfur containing brightener to improve the quality of the alloy deposit. Improvements in the alloy deposit include improving
10 such characteristics such as one or more of the brightness of the deposited alloy, the luster of the deposited alloy, the levelness of the deposited alloy, the hardness of the deposited alloy, the reflectivity of the deposited alloy, and the similarity in appearance to a high quality chromium deposit. General examples of sulfur containing brighteners include sulfinic acids, sulfonic acids, aromatic
15 sulfonates, aromatic sullfinates, sulfonamides, sulfonimides, sulfimides, sulfo-
betaines, and the water-soluble salts of these materials. Examples sulfur containing brighteners include the alkyl naphthalene and benzene sulfonic acids, the benzene and naphthalene di- and trisulfonic acids, benzene and naphthalene sulfonamides, and sulfonimides such as saccharin, vinyl and allyl sulfonamides
20 and sulfonic acids.

Specific examples of sulfur containing brighteners include sodium saccharinate; trisodium 1,3,6-naphthalene trisulfonic acid; trisodium 1,3,7-naphthalene trisulfonic acid; benzene sulfinic acid; sodium styrene sulfonate; p-toluene sulfinic acid; p-toluene sulfonic acid; propyl sulfonic acid;
25 beta-hydroxy propyl sulfonic acid; ditolylsulfimide; sodium salt of di-o-tolyl disulfimide; sodium salt of dibenzene disulfimide; pyridine-3-sulfonic acid; p-vinylbenzene sulfonic acid; sodium allyl sulfonate; sodium vinyl sulfonate; sodium propargyl sulfonate; sodium o-sulfobenzimide; disodium 1,5-naphthalene disulfonate; sodium benzene monosulfonate; dibenzene sulfonimide; sodium

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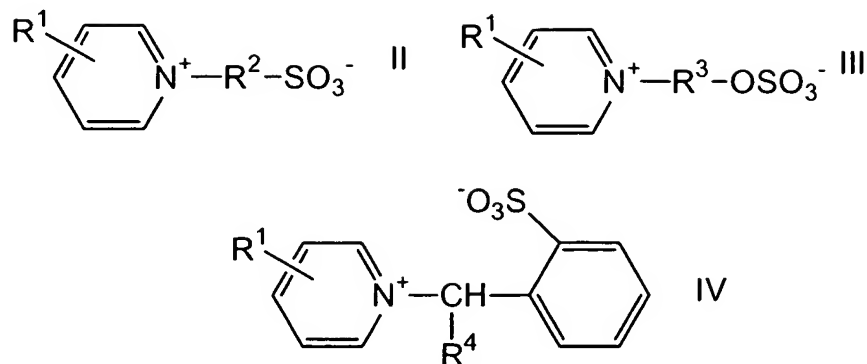
benzene monosulfinate; sodium allyl sulfonate; sodium
3-chloro-2-butene-1-sulfonate; monoallyl sulfamide; diallyl sulfamide;
1(gamma-sulfopropoxy)-2-butyne-4-ol; 1,4-di(beta-hydroxy-gamma-sulfonic
propoxy)-2-butyne; allyl sulfonamide; quinaldyl-N-propanesulfonic acid betaine;
5 quinaldine dimethyl sulfate; isoquinaldyl-N-propanesulfonic acid betaine;
isoquinaldine dimethyl sulfate; disulfonated 1,4-di(beta-hydroxyethoxy)-2-butyne;
and sulfonated 1-(beta-hydroxyethoxy)-2-propyne. Many sulfur containing
brighteners are described in U.S. Patent 3,922,209; 4,036,709; 4,053,373; and
4,421,611 which are hereby incorporated by reference.

10 Sulfo-betaines are heterocyclic compounds having Formula I:



wherein RN is an aromatic heterocyclic nitrogen-containing group, and R' is an
alkylene or hydroxy alkylene group. Generally, the RN group is an aromatic
nitrogen-containing group such as pyridine, substituted pyridines, quinoline,
15 substituted quinolines, isoquinoline, substituted isoquinolines, benzimidazoles,
and acridines. Various substituents can be incorporated into the aromatic
nitrogen-containing groups specified above, and the substituent may be attached
to the various positions of the aromatic group. Examples of substituents include
hydroxy, alkoxy, halide, lower alkyl, lower alkenyl, amino alkyl, mercapto, cyano,
20 hydroxyalkyl, acetyl, benzoyl, etc.

The sulfo-betaine compounds can also be characterized by Formulae II,
III, and IV:

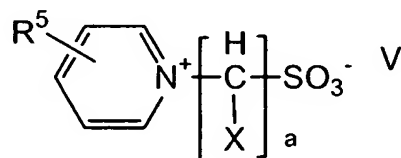


wherein R¹ is hydrogen, benzo(b), or one or more lower alkyl, halide, hydroxy, lower alkenyl or lower alkoxy groups; R² is an alkylene or hydroxy alkylene group containing three or four carbon atoms in a straight chain; R³ is an alkylene or hydroxy alkylene group containing two or three carbon atoms in a straight chain; and R⁴ is a hydrogen or a hydroxyl group.

As indicated in Formulae II, III, and IV, the sulfobetaines contain a pyridinium portion which may be an unsubstituted pyridine ring or a substituted pyridine ring. Thus, R¹ may be one or more lower alkyl groups, halogen groups, lower alkoxy groups, hydroxy groups or lower alkenyl groups.

Examples of the pyridine groups which may be included in the above Formulae II-IV include pyridine, 4-methyl pyridine (picoline), 4-ethyl pyridine, 4-t-butyl pyridine, 4-vinyl pyridine, 3-chloro pyridine, 4-chloro pyridine, 2,3 or 2,4 or 2,6 or 3,5-di-methyl pyridine, 2-methyl-5-ethyl pyridine, 3-methyl pyridine, 3-hydroxy pyridine, 2-methoxy pyridine, and 2-vinyl pyridine.

In Formula II, R² can be an alkylene or hydroxy alkylene group containing three or four carbon atoms in a straight chain which may contain alkyl substituents which may be represented by Formula V

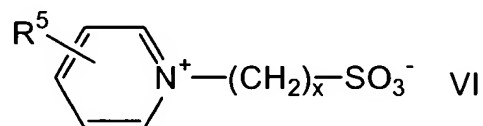


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wherein R⁵ is hydrogen or a lower alkyl group, one X is hydrogen, hydroxy or a hydroxy methyl group, the remaining X is hydrogen and a is 3 or 4.

The preparation of the sulfo-betaines of Formula II wherein R² is an alkylene radical is described in, for example, U.S. Patent 2,876,177, which is hereby incorporated by reference. Briefly, the compounds are formed by reaction of pyridine or a substituted pyridine with lower 1,3- or 1,4-alkyl sultones. Examples of such sultones include propane sultone and 1,3- or 1,4-butane sultone. The reaction products formed thereby are internal salts of quaternary ammonium-N-propane-omega-sulfonic acids or the corresponding butane derivative, depending on the alkyl sultone used.

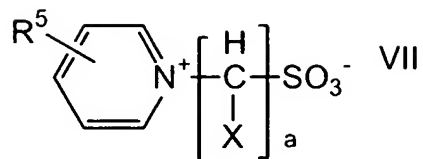
Examples of sulfo-betaines of Formula II wherein R² is an alkylene group may be represented by Formula VI:



wherein R⁵ is hydrogen, one or more lower alkyl groups or a benzo(b) group, and x is 3 or 4.

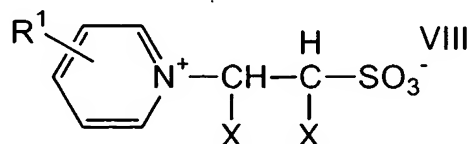
The preparation of the sulfo-betaine of Formula II wherein R² is a hydroxy alkylene group is described in, for example, U.S. Patent 3,280,130, which is hereby incorporated by reference. The method involves a first reaction step wherein pyridine is reacted with epichlorohydrin in the presence of hydrochloric acid, and, thereafter, in a second reaction step, the quaternary salt formed thereby is reacted with sodium sulfite.

Examples of the sulfo-betaines wherein R² is a hydroxy alkylene group including pyridine compounds of the Formula VII:



wherein R⁵ is hydrogen, one or more lower alkyl groups or a benzo(b) group, a is 3 or 4, one X substituent is a hydroxyl group and the other are hydrogen. In an alternative embodiment, two of the X groups could be hydrogen and the third X group can be a hydroxy alkyl group, such as a hydroxy methyl group.

5 The sulfo-betaines include the type represented by Formula III above wherein R¹ is defined as in Formula I, and R³ is an alkylene or hydroxy alkylene group containing two or three carbon atoms in a straight chain and optionally pendant hydroxyl groups, hydroxyl alkyl groups or alkyl groups containing one or two carbon atoms. Examples of the betaines represented by Formula III are
10 those wherein R¹ includes pyridine compounds of Formula VIII:



wherein R¹ is hydrogen, a lower alkyl group or a benzo(b) group, and both X groups are hydrogen or one X is hydrogen and the other is a hydroxyl group.

The preparation of the sulfo-betaines of the type represented by Formulae III and VIII which are known as pyridinium-alkane sulfate betaines is known in
15 the art. For example, the sulfate betaines can be prepared by reacting a pyridine compound with an alkanol compound containing a halogen atom to form an intermediate hydroxylalkyl pyridinium-halide which is thereafter reacted with the corresponding halosulfonic acid to form the desired betaine. Specifically,
pyridinium-(ethyl sulfate-2) betaine can be prepared by reacting ethylene
20 chlorohydrin with pyridine followed by reaction with chlorosulfonic acid. The

TASKP104US

details of the procedure are described in U.S. Patent 3,314,868 which is hereby incorporated by reference. Other alkanol compounds containing a halogen which can be reacted with pyridine to form the desired betaines include 1-chloro-2-propanol, 3-chloro-1-propanol, etc.

5 Betaines also include those represented by Formula IV given above which may be obtained by reacting, for example, o-chloro benzyl chloride (prepared from o-chloro benzaldehyde) with pyridine or a substituted pyridine followed by replacement of the o-chloro group with a sulfonic acid group. Although a similar
10 compounds, the ortho derivative tend to perform better in the electroplating baths of the present invention.

 In another embodiment, the quaternary alloy electroplating baths contain an effective amount of at least one organic brightener to improve the quality of the alloy deposit. General examples of organic brighteners include acetylenic
15 alcohols, ethylenic alcohols, acetylenic amines, acetylenic esters, acetylenic sulfonic acids and sulfonates, alkoxylated acetylenic alcohols such as ethoxylated and propoxylated acetylenic alcohols, acetylenic carboxylic acids such as 3-(2-propynoxy)-2-propenoic acid, coumarins, aldehydes, compounds containing the $C\equiv N$ linkage, and N-heterocyclics.

20 Specific examples of organic brighteners include ethoxylated butynediol; 2-butyne-1,4-diol; propargyl alcohol; thiodipropionitrile; ethoxylated propargyl alcohol; hydroxyethyl propynyl ether; beta-hydroxypropyl, propynyl ether; gamma-propynoxy, gamma-propynoxy, bis-beta-hydroxyethyl ether 2-butyne-1,4-diol; bis-beta-hydroxypropyl ether 2-butyne-1,4-diol; 1,4-di-(beta-hydroxyethoxy)-2-butyne; 1,4-di-(beta-hydroxy-gamma-chloropropoxy)-2-butyne;
25 1,4-di-(beta-gamma-epoxypropoxy)-2-butyne; 1,4-di-(beta-hydroxy-gamma-butenoxy)-2-butyne; 1,4-di-(2'-hydroxy-4'-oxa-6'-heptenoxo)-2-butyne; N-(2,3-dichloro-2-propenyl)-pyridinium chloride; 2,4,6-trimethyl N-propargyl

TASKP104US

pyridinium bromide; N-allylquinaldinium bromide; 2-methyl-3-butyn-2-ol; N-allylpyridinium bromide; N-allylisoquinaldine bromide; 1-(beta-hydroxyethoxy)-2-propyne; 1-(beta-hydroxypropoxy)-2-propyne; phenosafranin; and fuchsin. Many acetylenic derivatives that may be employed as organic brighteners in the quaternary alloy electroplating baths include those described in the U.S. Patents 3,133,006; 3,140,988; 3,152,975; 3,160,574; 3,170,853; 3,305,462; 3,366,557; 3,699,016; 3,378,470; 3,502,550; 3,515,652; 3,711,384; 3,719,568; 3,723,260; 3,759,803; 3,795,592; 3,860,638; 3,862,019; 3,844,773; 3,898,138; 3,907,876; 3,969,198; 4,036,709; 4,054,495; 4,062,738; and 4,421,611, which are hereby incorporated by reference.

The electroplating baths may optionally contain one or more of a number of additives. Such additives include complexing agents, chelating agents, surfactants, wetting agents, hardening agents, pH adjusters, leveling agents, reducing agents, antipitting agents, promoters, antioxidants, stress relief agents, conductivity salts, and the like. In one embodiment, the electroplating baths contain from about 0.001% to about 5% by weight of each of the additives.

In embodiments where the quaternary alloy contains iron, the electroplating bath optionally contains one or more bath-soluble complexing agents for iron. Such complexing agents may be amine-containing complexing agents or aliphatic carboxylic acids containing from about 1 to about 3 carboxyl groups and from about 1 to about 6 hydroxyl groups. The carboxyl group may be present as -COOH, as the anion -COO⁻ in solution, or in the form of an internal lactone such as present in the sugars. Examples of complexing agents in the hydroxy substituted lower aliphatic carboxylic acids having from about two to about eight carbon atoms include ascorbic acid, isoascorbic acid, citric acid, malic acid, glutaric acid, gluconic acid, muconic acid, glutamic acid, glycollic acid, aspartic acid, dextrose, sucrose, and the like. Examples of amine-containing complexing agents include nitrilotriacetic acid and ethylene diamine tetra-acetic acid. Alternative complexing agents include water soluble salts of ammonium,

TASKP104US

alkali metal, and iron salts.

5 The complexing agents facilitate keeping the metal ions, particularly the ferrous and ferric ions, in solution thereby preventing precipitation of iron as ferric hydroxide. In one embodiment, the electroplating bath contains from about 5 to about 100 grams/liter of the complexing agent to provide a mole ratio of complexing agent to iron ions in the bath of from about 1:1 to about 50:1.

10 The optional incorporation of wetting or surface active agents (surfactants) and particularly anionic wetting agents into the electroplating baths of the invention sometimes results in a ternary alloy plating with improved leveling and brightness, and/or the electroplating baths exhibit improved stability compared to an electroplating bath without wetting or surface active agents. The incorporation of surfactants may in some instances mitigate gas streaking and pitting.

15 Wetting agents promote leveling and brightening, as well as promoting bath stability. Examples of wetting agent include polyoxyalkylated naphthols; ethylene oxide/polyglycol compounds; sulfonated wetting agents; carbowax type wetting agents; and the like.

20 Surfactants contribute to the overall stability of the bath and improve various properties in the resultant tin alloy layer. General examples of surfactants include one or more of a nonionic surfactant, cationic surfactant, anionic surfactant, and amphoteric surfactant. Specific examples of surfactants include nonionic polyoxyethylene surfactants; alkoxylated amine surfactants; ethylene oxide-fatty acid condensation products; polyalkoxylated glycols and phenols; betaines and sulfobetaines; amine ethoxylate surfactants; quaternary ammonium salts; pyridinium salts; imidazolinium salts; sulfated alkyl alcohols; 25 sulfated lower ethoxylated alkyl alcohols; sodium lauryl sulfonate; sodium sulfate derivative of 2-ethyl-1-hexanol and sodium dialkyl sulfosuccinates such as the dihexyl ester of sodium sulfosuccinic acid; and the like.

The optional incorporation of leveling agents in some instances promotes

TASKP104US

the formation of a smooth surface of the electroplated tin alloy layer, even if the cathode surface on which the tin alloy layer is formed is not smooth. Examples of leveling agents include the condensation products of thiourea and aliphatic aldehydes; thiazolidinethiones; imidazolidinethiones; quaternized polyamines; and the like. Specific examples of leveling agents include 1-(sulfopropyl)pyridinium hydroxide and (1-sulfo-2-hydroxypropyl)pyridinium hydroxide.

Suitable hardening agents include 2-butyne-1,4-diol, phenylpropionic acid, 2-butyne-1,4-disulfonic acid, 3-dimethylamino-1-propyne and bis(trimethylamine)-1,2-diphenyl-1,2-bis(dichloroboryl)ethylene. The hardener effectively makes grain size more fine and slows down the rate at which the nickel, cobalt, and at least two alloy metal ions reach the substrate. This thereby provides a more uniform deposition of the coating on the substrate.

The optional incorporation of one or more conductivity salts in some instances enhances the conductivity of the electroplating solution, such as by varying the chloride content or by the addition of conductivity salts. In one embodiment, such conductivity salts are added during make up of the electroplating bath. Examples of conductivity salts include boric acid, sodium sulfate, sodium chloride, potassium sulfate, potassium chloride, and the like. Higher conductivity generally means that lower operating electrical costs are realized. It also may allow the application of more current from rectifiers with lower voltage maximums. Finally, higher conductivity may allow for improved current carrying capacity into confined plating spaces. In one embodiment, the electroplating bath contains from about 5 g/L to about 200 g/L of a conductivity salt. In another embodiment, the electroplating bath contains from about 10 g/L to about 150 g/L of a conductivity salt.

In one embodiment, a catalyst is not included in the electroplating bath. In another embodiment, a chromium compound is not included in the electroplating bath. In yet another embodiment, a cyanide compound is not

TASKP104US

included in the electroplating bath. In still yet another embodiment, a lead compound is not included in the electroplating bath. In these embodiments, the electroplating bath is environmentally friendly.

5 The pH of the electroplating bath is maintained to promote the efficient plating of the quaternary alloy on the substrate/cathode. In one embodiment, the pH of the electroplating bath is about 2 or more and about 6 or less. In another embodiment, the pH of the electroplating bath is about 3 or more and about 5 or less. In yet another embodiment, the pH of the electroplating bath is about 3.5 or more and about 4.5 or less. The pH of the electroplating bath may be
10 adjusted using additions of the acid or a base compound. The acids are relatively strong acids that are not oxidizing acids. Examples of acids include sulfuric acid, trifluoroacetic acid, phosphoric acid, polyphosphoric acid, fluoboric acid, hydrochloric acid, acetic acid, alkane sulfonic acids, and alkanol sulfonic acids. Bases include hydroxide compounds, such as ammonium hydroxide,
15 tetraalkylammonium hydroxide, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, lithium carbonate, nickel carbonate, cobalt carbonate, lithium bicarbonate, nickel bicarbonate, cobalt bicarbonate, and the like.

20 The temperature of the electroplating bath is maintained to promote the efficient plating of the quaternary alloy on the substrate/cathode. In one embodiment, the temperature of the electroplating bath, during plating, is about 10° C. or more and about 90° C. or less. In another embodiment, the temperature of the electroplating bath is about 30° C. or more and about 80° C. or less. In yet another embodiment, the temperature of the electroplating bath is
25 about 40° C. or more and about 70° C. or less.

Any suitable source of power is connected to the electrodes, such as direct current, alternating current, pulsed current, periodic reverse current, or combinations thereof. A current density is imposed from an energy source through the electrodes causing nickel, cobalt, and at least two alloy metal ions

TASKP104US

from the electroplating bath to migrate towards and attach to the substrate/cathode forming a layer of a nickel, cobalt, and at least two alloy metals thereon. In one embodiment, current densities of about 1 ASF or more and about 500 ASF or less are employed. In another embodiment, current
5 densities of about 5 ASF or more and about 200 ASF or less are employed. In yet another embodiment, current densities of about 10 ASF or more and about 100 ASF or less are employed. In still yet another embodiment, current densities of about 2 ASF or more and about 40 ASF or less are employed. In still yet another embodiment, current densities of about 4 ASF or more and about 35
10 ASF or less are employed.

Circulation of the bath in the tank is optionally provided by any suitable means, such as a filtration system and/or air agitation system. Circulation and agitation facilitates keeping the anodes active, and provides benefits to the quaternary alloy forming reaction by keeping ion concentrations substantially
15 equal in all areas of the electroplating bath, and in some instances contributes to the resultant brilliant appearance of the alloys. For example, a pump may continuously or intermittently, as needed, pump the electroplating bath through a filter to provide the circulation and to remove contaminants and any other particles which may undesirably precipitate out of the electroplating bath. An air
20 agitation system also may operate to circulate the solution in the electroplating bath. The components of the electroplating bath may be replenished as necessary to facilitate the electroplating process.

The length of time that the substrate/cathode is in contact with the electroplating bath under a specified current density depends upon the desired
25 thickness of the resultant quaternary alloy layer and the concentrations of the electroplating bath components. In one embodiment, the substrate/cathode is in contact with the electroplating bath (period of time from the when the nickel, cobalt, and at least two alloy metals begin to form until the quaternary alloy is removed from the bath) under a specified current density for a time of about 1

TASKP104US

second or longer and about 120 minutes or shorter. In another embodiment, the substrate/cathode is in contact with the electroplating bath (under plating conditions) under a specified current density for a time of about 5 seconds or longer and about 60 minutes or shorter. In yet another embodiment, the
5 substrate/cathode is in contact with the electroplating bath (under plating conditions) under a specified current density for a time of about 10 seconds or longer and about 30 minutes or shorter.

The quaternary alloy electroplating bath optionally contains at least one selective membrane, such as ionic and nonionic selective membranes,
10 positioned between the anode and cathode. The membranes may function as diffusion barriers. The presence of a selective membrane forms a catholyte around the cathode and an anolyte around the anode, where the catholyte is typically the electroplating bath. Selective membranes may have one or more of the following properties: permit the passage therethrough of certain ionic species
15 while preventing the passage therethrough of other ionic species; permit the passage therethrough of nonionic species while preventing the passage therethrough of ionic species; prevent or mitigate the migration of additives of the catholyte to the anode; and/or prevent substantial amounts of metal cations from migrating from the catholyte to the anolyte. For example, the selective
20 membrane may permit the flow of water therethrough, for instance osmotically, while preventing the passage of metal ions therethrough. In some instances, the migration of additives of the catholyte to the anode may produce undesirable species at the anode.

The electroplating bath, and valves that permit components to enter the
25 electroplating bath may be equipped with flow meters and/or flow controllers to measure and control the amount of components entering into the electroplating bath. The flow meter and/or a flow controller may be connected to a computer/processor including a memory to facilitate measuring and controlling the amount of individual components that flow into the electroplating bath and/or

TASKP104US

for automated process control of the ternary alloy electroplating method. The computer/processor may be further coupled to sensors in the electroplating bath to measure one or more of pH, species concentration, volume, and the like. The computer/processor may be coupled to control valves that permit introduction of additional water, metals, anode replacement, acid, and/or base, into the electroplating bath.

Referring to Figure 1, an exemplary arrangement of a method and nickel cobalt quaternary alloy plating system are described. The quaternary alloy plating system 100 includes a power source (not shown) for providing current to an electrochemical cell 102 containing an aqueous bath. The electrochemical cell 102 may contain an optional selective membrane 106, which subdivides the bath into a catholyte or electroplating bath 108 and an anolyte 110 (and this general arrangement may be repeated one or more times in an adjacent fashion to provide multiple electrochemical cells with a plurality of anolytes 110, catholytes 108, and selective membranes 106). The catholyte or electroplating bath 108 contains the ionic metals as described above while the anolyte 110 contains any acidic, basic, or neutral solution that can carry a current. The quaternary alloy plating system 100 also contains an anode 112 and a cathode 114. Current is run through the electrochemical cell 102 inducing the deposition or plating of a nickel cobalt quaternary alloy at the cathode 110. If the optional selective membrane 106 is not present, which occurs in a more traditional set-up, there is no separate anolyte and catholyte, but only an electroplating bath in the electrochemical cell 102.

Optionally, after the quaternary alloy is formed, the quaternary alloy may be heat treated to improve its hardness. For example, the nickel cobalt quaternary alloy may be heated from about 200 °C. to about 700 °C., and more specifically from about 250 °C. to about 550 °C., for a sufficient period of time to improve hardness.

The quaternary alloys formed in accordance with the present invention

TASKP104US

contain a major amount of nickel and cobalt and minor amount of at least two alloy metals. Major amounts include at least 50% by weight whereas minor amounts include less than 50% by weight.

5 Examples of quaternary alloys that may be formed in accordance with the present invention include nickel cobalt boron iron alloys, nickel cobalt bismuth iron alloys, nickel cobalt tin iron alloys, nickel cobalt copper iron alloys, nickel cobalt silver iron alloys, nickel cobalt bismuth boron alloys, nickel cobalt tin boron alloys, nickel cobalt copper boron alloys, nickel cobalt silver boron alloys, nickel cobalt boron iron silver alloys, and the like. In one embodiment, the quaternary alloys contain at least four metals. In another embodiment, the quaternary alloys contain at least five metals.

10 The quaternary alloy formed in accordance with the present invention mainly contains nickel, cobalt, and at least two alloy metals. In one embodiment, the quaternary alloy contains from about 30 % to about 80 % by weight of nickel, from about 30 % to about 80 % by weight of cobalt, and from about 0.001 % to about 10 % by weight of each of at least two alloy metals. In another embodiment, the quaternary alloy contains from about 40 % to about 70 % by weight of nickel, from about 40 % to about 70 % by weight of cobalt, and from about 0.01 % to about 5 % by weight of each of at least two alloy metals.

15 While the quaternary alloy formed in accordance with the present invention mainly contains nickel, cobalt, and at least alloy metals, other components may be present including small amounts (such as less than about 2 % by weight) of other compounds. For example, the quaternary alloy may contain small amounts of one or more of the additives to the bath, contaminants, or another metal. In another embodiment, the quaternary alloy formed in accordance with the present invention contains less than about 1 % by weight of other components (not nickel, cobalt, or at least two alloy metals). In yet another embodiment, the quaternary alloy formed in accordance with the present invention contains less than about 0.1 % by weight of other components.

TASKP104US

The nickel cobalt quaternary alloy formed in accordance with the present invention, can have a thickness as small as about 0.5 μm with substantially no pores. In another embodiment, the thickness of the quaternary alloy formed in accordance with the present invention can be as small as about 1 μm with substantially no pores.

The nickel cobalt quaternary alloys formed in accordance with the present invention may have high hardness values, when measured using a Vickers hardness measuring device having 100 gm loads. In one embodiment, the hardness of the quaternary alloy formed in accordance with the present invention is at least about 600 as deposited, and at least about 900 after optional heat treatment. In another embodiment, the hardness of the quaternary alloy formed in accordance with the present invention is at least about 1,000 as deposited, and at least about 1300 after optional heat treatment. In yet another embodiment, the hardness of the quaternary alloy formed in accordance with the present invention is at least about 1,050 as deposited, and at least about 1400 after optional heat treatment.

The resultant nickel cobalt quaternary alloy layer electroplated in accordance with the present invention has many desirable characteristics including one or more of high brightness, high hardness, excellent lubricity, corrosion resistance, uniform thickness, excellent leveling, excellent ductility, lack of pinholes, environmentally friendly processing, and controllable thickness.

Uniform thickness means uniform in two senses. First, a uniformly thick quaternary alloy layer results when electroplating a smooth or curvilinear surface cathode and the nickel cobalt quaternary alloy layer has substantially the same thickness in any location after removal from the surface of the cathode. This uniformly thick quaternary alloy layer is smooth and flat when the surface of the cathode is smooth while the uniformly thick quaternary alloy layer may have an uneven surface mimicking the uneven contours of the underlying cathode surface. Second, a uniformly thick quaternary alloy layer results when

TASKP104US

electroplating an uneven cathode surface so that the resultant nickel cobalt quaternary alloy layer appears smooth and the quaternary alloy layer has substantially the same thickness within locally smooth regions on the surface of the cathode. This second sense also refers to excellent leveling.

- 5 While the invention has been explained in relation to certain embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.